300. *Lead Alunite.*

By Henry Bassett.

A preparation of lead alunite has been obtained which contains 44% of $Pb[Al_2(OH)_4(H_2O)_2][SO_4]_2$ mixed with $H_2O[Al_3(OH)_5H_2O][SO_4]_2$ and a little $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2$. This gives valuable support to the view that in the alunite lattice one-third of the aluminium positions can be vacant.

Alunite, $K[Al_3(OH)_6][SO_4]_2$ is the first and best-known member of a group of minerals in which isomorphous replacement of a very varied character can occur (Hendricks, *Amer. Min.*, 1937, **22**, 772). Such replacement can be of the simple type ($K^{\cdot}$ by $NH_4^{\cdot}$, $Na^{\cdot}$, $Rb^{\cdot}$; $Al^{\cdot\cdot\cdot}$ by $Fe^{\cdot\cdot\cdot}$) or of a compensatory nature. The latter type of replacement is found in some minerals of the alunite group which contain lead, strontium, or barium in place of alkali metal. The extra positive charge of the bivalent metal is balanced by replacement of some of the SO_4'' by PO_4''' or AsO_4'''. Hinsdalite, $Pb[Al_3(OH)_6][SO_4][PO_4]$ is of this nature. Plumbojarosite is considered by Hendricks to be $Pb[Fe_3(OH)_6]_2[SO_4]_4$ with one of the potassium positions vacant.

The $Al_3(OH)_6$ or $Fe_3(OH)_6$ is part of an endless band of AlO_6 or FeO_6 octahedra in which each Al or Fe ion is surrounded by four hydroxyl ions and by two oxygen atoms of SO_4 ions. The latter are in *trans*-positions in the octahedra which are joined by their edges, two hydroxyl ions being shared by two octahedra.

Hendricks showed that one of the six hydroxyl ions could be replaced by a water molecule but as the $[Al_3(OH)_5H_2O]$ group carried four positive charges no potassium ion is required to balance the charges on the two SO_4 ions. The place of the potassium in the crystal lattice is therefore taken by another water molecule.

According to the results of Bassett and Goodwin (*J.*, 1949, 2254) more than one of the six hydroxyl ions can be replaced by water molecules if one of the three octahedral postions contains no $Al^{\cdot\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$. There originate in this way compounds such as $K[Al_2(OH)_3(H_2O)_3][SO_4]_2$, $H_2O[Al_2(OH)_2(H_2O)_4][SO_4]_2$, and $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2$. Most members of the alunite group containing $Pb^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, or Ba contain phosphate (or arsenate) in addition to sulphate, but it would seem from the above that a compound $Pb[Al_2(OH)_4(H_2O)_2][SO_4]_2$ should be obtainable and be a true alunite. The existence of this compound would give strong additional support to the view that vacant octahedral positions can occur in the alunite lattice.

A preparation has been obtained which according to the analysis contains about 44% of alunite with the above formula, the remainder consisting chiefly of $H_2O[Al_3(OH)_5H_2O][SO_4]_2$. It gives an excellent *X*-ray diagram of alunite and is much less soluble than is lead sulphate, just as the normal alunites are much less soluble than the alkali-metal sulphates.

It is possible that some modification of the preparative procedure might give a product with a composition nearer to that of pure $Pb[Al_2(OH)_4(H_2O)_2][SO_4]_2$. This is not at all certain, however, since isomorphous replacement by $H_2O[Al_3(OH)_5H_2O][SO_4]_2$ and $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2$ occurs so readily. The author is not able at present to carry out further experiments to settle this point.

Attempts to prepare calcium, strontium, and barium alunites in a similar way to the lead compound gave products which are probably mixtures of the desired alunites and the corresponding sulphates. It has not been possible to attempt to separate these.

Similar experiments with basic aluminium sulphate solutions to which manganese, nickel or cadmium salts had been added gave relatively small amounts of precipitates consisting of the glassy solid of Two-liquid System I of the system Al_2O_3–SO_3–H_2O (Bassett and Goodwin, *loc. cit.*, p. 2257). Only the precipitate from the cadmium experiment was actually analysed. It was easily soluble in dilute acid and contained no cadmium. The ionic radii of these three metals are not greatly different from those of the alkali and alkaline-earth metals and for that reason it seemed worth while to see whether they could yield alunites. If these existed they would probably be soluble with difficulty in acids.

EXPERIMENTAL.

A basic aluminium sulphate solution was prepared from N-sulphuric acid (100 c.c.), aluminium (1·232 g.), and a drop of mercury. The finely divided mercury was removed by filtration and a solution of lead nitrate (3·178 g.) in water (20 c.c.) slowly added with vigorous stirring to the boiling mixture. This is the amount of lead nitrate which would have been needed to precipitate all the $Al_2(OH)_4SO_4$ as alunite if the basic solution was considered to contain only $Al_2(OH)_4SO_4$ and $Al_2(SO_4)_3$.

The mixture was heated on a hot plate to about 75° for 4 weeks with occasional stirring and replacement of water lost by evaporation. The precipitate was then filtered off on a hardened filter paper on a Buchner funnel and washed with cold water (75 c.c.), followed by rectified spirit (25 c.c.), and weighed 6·02 g. after being dried in the air.

Under the microscope the solid was seen to consist apparently of a mixture of very minute prisms of lead sulphate and minute square crystals of alunite. Its *X*-ray diagram showed the lines of these two compounds. Treatment at room temperature with 2N-hydrochloric acid removed all the free lead sulphate. Extraction of 1 g. of the solid with 25 c.c. of the 2N-acid for 3½ hours removed lead sulphate representing 26·6% of the original solid, and a further 25 c.c. during 24 hours removed a further quantity equivalent to only 1·9% of the original solid. The extracts contained only a trace of alumina. The residual material appeared to consist of very minute square crystals with a high double refraction. No prisms of lead sulphate could be detected. It gave an excellent alunite *X*-ray diagram which showed none of the lead sulphate lines. It was quite free from chloride, which showed that there had been no replacement of hydroxyl by chlorine during the treatment with hydrochloric acid.

Method of Analysis.—Owing to its insolubility in hydrochloric acid the lead alunite (air-dried) was analysed as follows : It was boiled for 15 minutes with aqueous sodium carbonate (1·5 g. in 15 c.c. of water for 0·2 g. of lead alunite), the mixture being well stirred and crushed several times with a glass rod. After the 15 minutes' boiling the mixture was diluted with boiling water (65 c.c.), allowed to cool, and set aside for 4 hours before filtration, and washing, with decantation, with about 100 c.c. of water. Solid on the paper was rinsed into the beaker in which most of the solid still remained and 10 c.c. of hot 2N-hydrochloric acid were poured through the filter into the beaker. This was sufficient to dissolve the precipitate completely, showing that attack of the alunite had been complete.

The alkaline filtrate from the lead carbonate was acidified with 2N-hydrochloric acid and a further 15 c.c. were added to the 200 c.c. of solution before precipitation of the sulphate. After removal of excess of barium from the barium sulphate filtrate the alumina in solution was precipitated with ammonia and weighed as Al_2O_3 after ignition at 1000—1100°. The precise nature of the lead compound obtained by the digestion with sodium carbonate is uncertain. It contains both lead and sodium carbonate but also more than half of the alumina originally present in the lead alunite. The lead in the acid solution was converted into sulphate by evaporation with sulphuric acid, and the lead sulphate filtered off and weighed on a sintered-glass Gooch crucible after drying at 100°. The alumina also present was precipitated with ammonia in the filtrate from the lead sulphate and weighed as Al_2O_3. The composition found by analysis was : PbO, 17·7; Al_2O_3, 29·9; SO_3, 34·7; H_2O (by difference), 17·7%. This composition can be expressed conveniently and very closely in terms of the mixture of alunites :

$$\begin{aligned}&Pb[Al_2(OH)_4(H_2O)_2][SO_4]_2,\ 44{\cdot}1;\\&H_2O[Al_3(OH)_5H_2O][SO_4]_2,\ 54{\cdot}35;\\&H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2,\ 1{\cdot}2\%.\end{aligned}$$

This leaves 0·35% of water unaccounted for, which may well have been adsorbed on the very fine solid. The solid is to be regarded as an essentially homogeneous solid solution with random distribution of the various ions or groups which can replace one another.

The *X*-ray examination of the lead alunite was made by Dr. G. B. Greenough, to whom I express my thanks.

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